

New Brønsted-Lewis Acidic Quaternary Ammonium Ionic Liquids: Synthesis, Acidity Determination and Acidity-Catalytic Activity Relationship

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A series of new Brønsted-Lewis acidic ionic liquids, which are operational simplicity, high stability, low cost and applicable for scaling up, have been synthesized and their activity for acetalization was examined. The comprehensive studies on the acidity-catalytic performance relationship of the Brønsted-Lewis acidic ionic liquids were performed. IR spectroscopy results confirmed that the new Brønsted-Lewis acidic ionic liquids possess both Brønsted and Lewis acid sites. The acidities were determined by Hammett method, and further studies on acidity-activity relationship revealed that the acidity played a key role in the acid-catalyzed probe reactions.

Keywords: Brønsted-Lewis acidic quaternary ammonium ionic liquids, Acid type, Acidity-catalytic activity relationship.

INTRODUCTION

Acid catalysis based on ionic liquids (ILs) has been considered to be very important because of the widespread use in synthetic and industrial chemistry¹⁻³. Both Lewis and Brønsted acid sites are significant for acid-catalyzed reactions, hence the ionic liquids functionalized with both Lewis and Brønsted acid sites should be more efficient. However, most reported acidic ionic liquids only possessed Brønsted or Lewis acidity. The works about the ionic liquids with dual Brønsted and Lewis acid sites are still rare.

The first ionic liquid system with both Lewis and Brønsted acidity was reported by Kou and Yang⁴, though a mixture, it was the sample completely constituting with ionic. Liu *et al.*^{5,6} documented the first real Brønsted-Lewis acidic ionic liquid, which was of good catalytic performance and reusability for the dimerization of rosin and fatty acid methyl ester. Similarly, a series of novel acidic ionic liquids consisting with double -SO₃H cations mediated zinc chloride were proved as mild and efficient catalysts for the Beckmann rearrangement⁷. Recently, Qi and Liang⁸ successfully prepared a novel ionic liquid with both Brønsted and Lewis acid sites. In this case, the ionic liquids exhibited high efficiency for the traditional acid-catalyzed reactions and the synergy of Lewis and Brønsted acid sites enhanced the activity. On the other hand, in order to understand the catalytic activity of the acidic ionic liquids, it is necessary to study the acidity. However, there are only few reports about the acidity and acidity-activity relationship of Brønsted-Lewis acidic ionic liquids^{5,9}.

In this work, we herein present a series of new Brønsted-Lewis quaternary ammonium acidic ionic liquids which are high stable, low cost, easily-prepared and applicability to large-scale reaction. The acid types and acidities of the new Brønsted-Lewis acidic ionic liquids were examined by IR spectroscopic probe method¹⁰ and the Hammett method¹¹ and the acidity-catalytic activity relationship was discussed.

EXPERIMENTAL

General procedure for the synthesis of Brønsted-Lewis acidic ionic liquids: Morpholine (8.7 g, 0.1 mol) and 1,4-butane sulfonate (13.6, 0.1 mol) were mixed in ethanol (50 mL) and heated under stirring for 5 h at 80 °C. The reaction was cooled down to room temperature. The white solid was filtered and washed for 3 times with ether, then dried at 80 °C for 5 h to afford the intermediate **1a** in 95 % yield. Concentrated sulfuric acid (0.05 mol) was added to the intermediate **1a** (0.05 mol) under ice-water bath and the mixture was stirred at 60 °C for 3 h to give a colourless liquid. Then, the liquid was dissolved in 5 mL deionized water and ZnO (0.025 mol) was added under stirring. After the solid was dissolved completely, removed solvent and dried under 100 °C for 5 h. The corresponding Brønsted-Lewis acidic ionic liquid was produced quantitatively. ¹H NMR (500 MHz, D₂O): δ 1.57 (d, 2H, *J* = 6.0 Hz), 1.65 (d, 2H, *J* = 8.5 Hz), 2.71 (t, 2H, *J* = 10 Hz), 2.95-3.00 (m, 4H), 3.29 (d, 2H, *J* = 6.0 Hz), 3.55 (t, 2H, *J* = 7.0 Hz), 3.87 (t, 2H, *J* = 7.5 Hz). IR (KBr, ν_{max}, cm⁻¹): 865, 1034, 1155, 1655, 3406.

[PSPip][SO₄]Zn: ¹H NMR (500 MHz, D₂O): δ 1.36-1.61 (m, 10H), 2.56-2.63 (m, 4H), 2.76 (t, 2H, *J* = 9.0 Hz), 3.17 (d, 2H, *J* = 9.0 Hz). IR (KBr, ν_{max}, cm⁻¹): 948, 1051, 1180, 1465, 1664, 3410 cm⁻¹.

Acetalization of aromatic aldehydes with diols: Aromatic aldehydes (0.1 mol), cyclohexane (10 mL), diols (0.15 mol) and the catalyst were mixed together in a three necked round bottomed flask equipped with a magnetic stirrer and Dean-Stark apparatus. The mixture was refluxed for 2 h. On completion, the catalyst was collected, washing with ether and drying in an oven at 80 °C for about 2 h.

Acidity evaluation by Hammett method with UV-visible spectroscopy: Water solutions of the ionic liquids were prepared from deionized water and the ionic liquids. All spectra were recorded with a UV757CRT spectrophotometer.

IR spectroscopy: Fourier transform infrared spectroscopy (FT-IR) was carried out on a VERTEX70 FT-IR spectrometer in the range of 4500-400 cm⁻¹. IR samples were prepared by mixing probe liquids and ionic liquids in a volume ratio of 2:5.

RESULTS AND DISCUSSION

Synthesis of Brønsted-Lewis acidic ionic liquids: Brønsted Lewis acidic ionic liquids were synthesized by three step synthesis route (**Scheme-I**). For this study, Brønsted-Lewis acidic ionic liquids having [PSMor] or [PSPip] cation, [SO₄] or [HPO₄] anion, together with Cu²⁺ or Zn²⁺ Lewis acid site were prepared. In the first step, the condensation of morpholine (Mor) or piperidine (Pip) and 1,4-butane sulfonate afforded intermediate **1a** or **2a**. Then, a stoichiometric amount of sulfuric acid or phosphoric acid was mixed with the intermediate to afford the homogeneous liquid phase **1b** or **2b**. In the third step, Lewis acid site was introduced to give the corresponding ionic liquids as shown in Fig. 1.

Catalytic properties of Brønsted-Lewis acidic ionic liquids: A comparative catalytic activity of different catalysts including concentrated sulfuric acid, *p*-toluenesulfonic acid, Brønsted-Lewis acidic ionic liquids as well as Brønsted/Lewis acidic ionic liquids was summarized in Table-1. The results demonstrated that the catalytic performances of Brønsted-Lewis acidic ionic liquids with the conjugate bases of SO₄²⁻ were better than those of ionic liquids with the conjugate bases of HPO₄²⁻, even concentrated sulfuric acid and PTSA under the same reaction conditions. Furthermore, it was noted that the

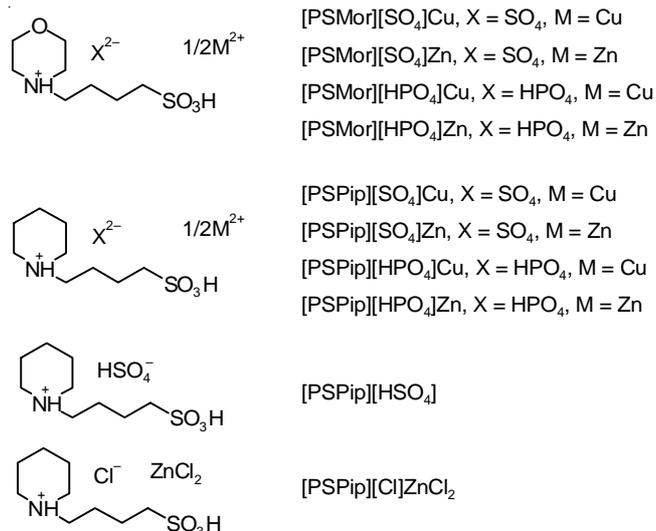
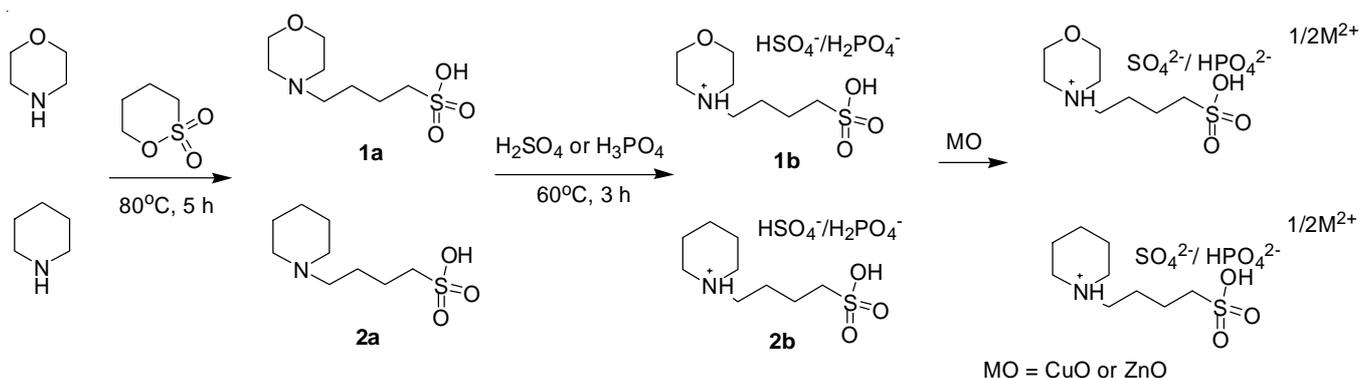


Fig. 1. Structures of Brønsted-Lewis acidic ionic liquids and Brønsted/Lewis acidic ionic liquids used in this paper

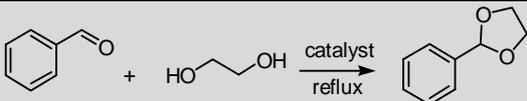
Brønsted-Lewis acidic ionic liquids exhibited the remarkably better catalytic activity than Brønsted/Lewis acidic ionic liquids (Table-1, entries 9 and 12). The synergy of both Brønsted and Lewis acid sites might enhance the activity⁸. All the Brønsted-Lewis acidic ionic liquids afforded good to excellent yields of products. [PSPip][SO₄]Zn was found to be the best catalyst for the acetalization, leading to 96 % yield of the desired product.

Compared with the traditional acidic catalysts, easy recycling is an attractive property of the acidic ionic liquid. Consequently, the catalytic activity of recycled [PSPip][SO₄]Zn was examined. [PSPip][SO₄]Zn could be reused for 6 times at least and there was no obvious decrease in yield of the product, which indicating that the new Brønsted-Lewis acidic ionic liquid was high efficient and recyclable catalyst for the acetalization. To ultimately discriminate the catalytic activities of various ionic liquids, their loadings should be decreased to real "catalytic amounts". The reactions were conducted with different catalyst loadings which ranged from 0.1 to 1.0 mol %. The yield of the product increased with the increase of the catalyst amount. Nearly quantitative yield was achieved when only 0.7 mol % of [PSPip][SO₄]Zn was used. Further increase of the catalyst loading led to no significant improvement in yield. Evidently it was enough to catalyze the acetalization efficiently at very low loading for [PSPip][SO₄]Zn.



Scheme-I: Synthesis route of Brønsted-Lewis acidic ionic liquids

TABLE-1
ACETALIZATION OF BENZALDEHYDE AND ETHANEDIOL^a



Entry	Ionic liquids	Catalyst dosage (mol %)	Recycle no.	Yield ^b (%)
1	[PSMor][SO ₄]Cu	1	-	92
2	[PSMor][SO ₄]Zn	1	-	94
3	[PSMor][HPO ₄]Cu	1	-	81
4	[PSMor][HPO ₄]Zn	1	-	81
5	[PSPip][SO ₄]Cu	1	-	91
6	[PSPip][SO ₄]Zn	1	1	96
7	[PSPip][HPO ₄]Cu	1	-	80
8	[PSPip][HPO ₄]Zn	1	-	81
9	[PSPip][HSO ₄]	1	-	89
10	H ₂ SO ₄	1	-	89
11	PTSA	1	-	86
12	[PSPip][Cl]ZnCl ₂	1	-	80
13	[PSPip][SO ₄]Zn	1	2	96
14	[PSPip][SO ₄]Zn	1	3	96
15	[PSPip][SO ₄]Zn	1	4	96
16	[PSPip][SO ₄]Zn	1	5	97
17	[PSPip][SO ₄]Zn	1	6	95
18	[PSPip][SO ₄]Zn	0.7	-	96
19	[PSPip][SO ₄]Zn	0.5	-	89
20	[PSPip][SO ₄]Zn	0.3	-	72
21	[PSPip][SO ₄]Zn	0.1	-	65

^aAll reactions were carried out under the Dean-Stark conditions: ethanediol (0.15 mol), benzaldehyde (0.1 mol) and cyclohexane (10 mL), refluxed. M²⁺ contents of the Brønsted-Lewis acidic ionic liquids used were all 50 %, ^bIsolated yield

Determination of acid type: Pyridine can be used as an IR spectroscopy probe to characterize the acidic type of solid acid and acidic ionic liquids¹¹. As shown in Fig. 2, after reacting with pyridine, the Brønsted-Lewis acidic ionic liquids samples had two new characteristic absorption peaks near 1540 and 1448 cm⁻¹, indicating that the new ionic liquids were of both Brønsted and Lewis acidity. Besides, these characteristic bands were essentially unchanged when pyridine was added to [PSMor][SO₄]Zn or [PSPip][SO₄]Zn, suggesting that morpholine or piperidine exhibited no obvious affect to the acidity. Furthermore, the higher characteristic Brønsted acid band wavenumber of [PSPip][SO₄]Zn than that of [PSPip][HPO₄]Zn resulted in a Brønsted acidity order: [PSPip][SO₄]Zn > [PSPip][HPO₄]Zn.

Acetonitrile, a weaker Lewis base than pyridine, was used as a probe to confirm the Lewis acidities of ionic liquids. It can be seen in Fig. 3 that, the new absorption peak at near 2330 cm⁻¹ appeared after acetonitrile was added to ionic liquids. This new peak was the characteristic peak of the CN-Lewis complex and when the intensity of Lewis acid increased, this new absorption peak moved to higher wavenumber. This result indicated that both [PSMor][SO₄]Zn and [PSMor][SO₄]Cu were of Lewis acidity. Comparing with that of [PSMor][SO₄]Cu, the characteristic peak of [PSMor][SO₄]Zn occurred blue shift, indicating that the Lewis acidity of [PSMor][SO₄]Zn was stronger than that of [PSMor][SO₄]Cu.

The IR spectra of [PSMor][SO₄]Zn with different Zn²⁺ contents were recorded and shown in Fig. 4. The wavenumber

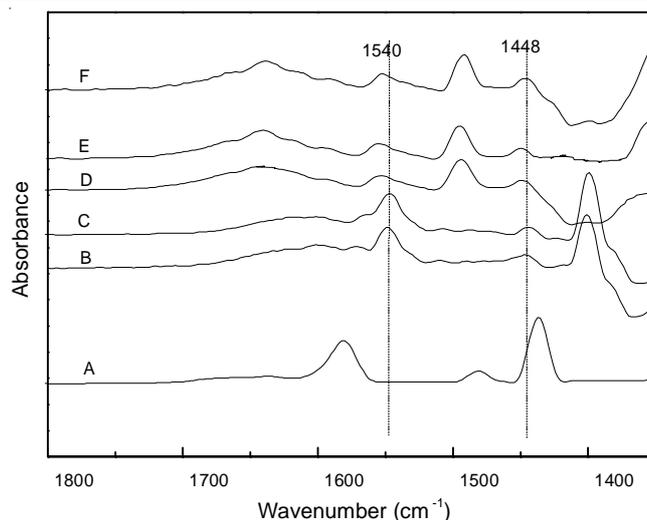


Fig. 2. FT-IR spectra of samples using pyridine as probe. A: pure pyridine; B: [PSPip][HPO₄]Zn; C: [PSPip][HPO₄]Cu; D: [PSMor][SO₄]Zn; E: [PSPip][SO₄]Zn; F: [PSMor][SO₄]Cu; (M²⁺ % = 50 %)

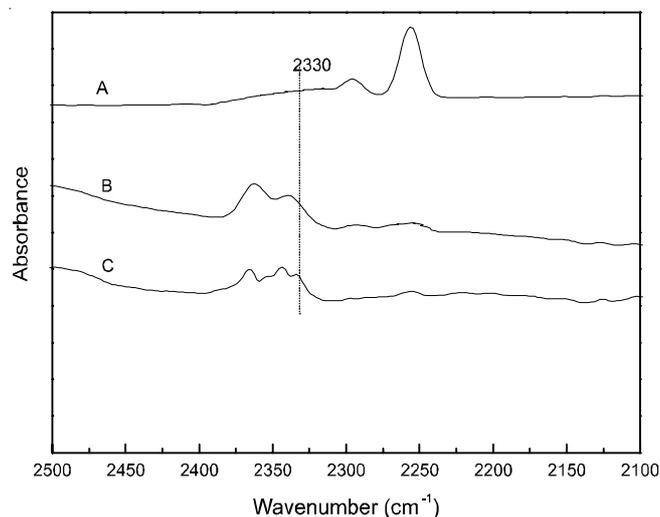


Fig. 3. FT-IR spectra of samples using acetonitrile as probe. A: pure acetonitrile; B: [PSMor][SO₄]Zn; C: [PSMor][SO₄]Cu; (M²⁺ % = 50 %)

changed from 1448 cm⁻¹ for 25 % Zn²⁺, to 1455 and 1448 cm⁻¹ for 50 % Zn²⁺, to 1460 and 1448 cm⁻¹ for 75 % Zn²⁺, which indicating that the Lewis acidity increased with the enhancement of Lewis acid site content. Moreover, a blue shift of the band near 1540 cm⁻¹ was also observed, suggesting that the Brønsted acidity also enhanced.

Determination of H₀ values: Acidities of the Brønsted-Lewis acidic ionic liquids were measured using UV-visible spectrophotometer with a basic indicator by Hammett method reported in the literatures^{10,12,13}. The acidities could be calculated by evaluating the protonation extent of uncharged indicator bases (named I) in the ionic liquids, in terms of the measurable ratio [I]/[IH⁺]. The Hammett function (H₀) is defined as:

$$H_0 = \text{pK}(\text{I})_{\text{aq}} + \log \left(\frac{[\text{I}]}{[\text{IH}^+]}\right)$$

where pK(I)_{aq} is the pK_a value of the indicator referred to an aqueous solution. The value H₀ can be regarded as the relative acidity of the ionic liquid.

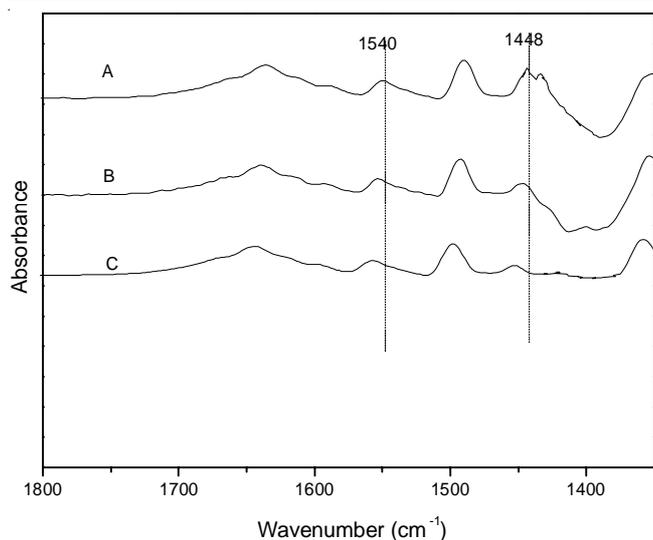


Fig. 4. FT-IR spectra of samples using pyridine as probe. A: [PSMor][SO₄]Zn (Zn²⁺ % = 25 %); B: [PSMor][SO₄]Zn (Zn²⁺ % = 50 %); C: [PSMor][SO₄]Zn (Zn²⁺ % = 75 %)

According to the values in Table-2, the acidity order of the nine ionic liquids was obtained: [PSPip][SO₄]ZnH⁺ ≈ [PSMor][SO₄]Zn > [PSPip][HSO₄] > [PSPip][SO₄]Cu > [PSMor][SO₄]Cu > [PSPip][HPO₄]Zn > [PSMor][HPO₄]Zn > [PSPip][HPO₄]Cu > [PSMor][HPO₄]Cu, which is in good agreement with the sequence of catalytic activity observed in acetalization (Table-1). Acid values of ionic liquids obtained

TABLE-2
H₀ AND ACIDITY VALUES OF BRØNSTED-LEWIS ACIDIC IONIC LIQUIDS

Entry	Ionic liquids	H ₀	Acid value (mg NaOH/mol)
1	[PSMor][SO ₄]Cu	1.25	88.3
2	[PSMor][SO ₄]Zn	1.20	108.8
3	[PSMor][HPO ₄]Cu	1.55	58.6
4	[PSMor][HPO ₄]Zn	1.43	73.3
5	[PSPip][SO ₄]Cu	1.26	85.8
6	[PSPip][SO ₄]Zn	1.21	113.9
7	[PSPip][HPO ₄]Cu	1.59	53.7
8	[PSPip][HPO ₄]Zn	1.40	78.2
9	[PSPip][HSO ₄]	1.22	85.1

using volumetric titration method are also consistent with the Hammett acidity trend for the same series of ionic liquids. Moreover, the acidities of ionic liquids with and without Lewis acid sites were all measured in order to understand the influence of Lewis acid sites to the Brønsted acidity obtained by Hammett method. The lower value of [PSPip][SO₄]Zn than that of [PSPip][HSO₄] suggested that the Brønsted acidity increased in presence of Lewis acid site. For this study, the Brønsted acidity of the ionic liquids depended on the cations, anions and Lewis acid sites. The comparatively high acidity was obtained when the Zn²⁺ was as Lewis acid site rather than Cu²⁺, which were in complete agreement with those determined using IR spectroscopy. In addition, the acidity of ionic liquid is the important property relevant to its catalytic activity for acid-

TABLE-3
ACETALIZATION OF VARIOUS ALDEHYDES WITH DIOLS CATALYZED BY [PSPip][SO₄]Zn.^a

Entry	Diols	Aldehydes	Product	Yield ^b (%)
1		Benzaldehyde		96
2	-	Phenyl acetaldehyde		95
3	-	<i>o</i> -Chloro benzaldehyde		94
4	-	Cyclamen aldehyde		96
5	-	<i>p</i> -Methoxy benzaldehyde		93
6	-	Cuminaldehyde		88
7		Piperonyl aldehyde		93
8	-	4-Formyl-benzonitrile		95
9	-	4-Methoxy benzaldehyde		91
10		Benzaldehyde		95
11	-	4-Methoxy benzaldehyde		89

^aAll reactions were carried out under the Dean-Stark conditions: diol (0.15 mol), aldehyde (0.1 mol), [PSPip][SO₄]Zn (0.7 mol %) and cyclohexane (10 mL), refluxed; ^bIsolated yield

catalyzed reactions¹⁴⁻¹⁷. In this work, we found that both catalytic activity and Brønsted acidity of the ionic liquid were significantly dependent on the anion. The acidity of the ionic liquid with HPO₄⁻ was weaker than that with SO₄²⁻. Meanwhile, the ionic liquids with SO₄²⁻ showed the best catalytic activity, and the activities of ionic liquids with HPO₄⁻ were poor.

Acetalization of aromatic aldehydes with diols catalyzed by [PSPip][SO₄]Zn: The acetalization of various aromatic aldehydes with diols showed clean conversion in high to excellent yields (Table-3). It was worth noting that the substitute group of the benzaldehyde was crucial to the yields of desired products¹⁸. The electron withdrawing groups might increase the reactivity of the reactant and enhance rate of acetal formation. Different diols including 1,2-ethanediol, 1,2-propylene glycol and neopentyl glycol were all converted to the corresponding products smoothly.

Conclusion

In summary, a series of new Brønsted-Lewis acidic ionic liquids were synthesized. Their catalytic activities in acetalization and acylation were examined and satisfactory results were obtained. Because of their superior character, such as operational simplicity, non-volatility, high stability and low cost, Brønsted-Lewis acidic ionic liquids could become the substitute of liquid inorganic acids in many cases of industrial application. IR spectroscopy indicated that the prepared Brønsted-Lewis acidic ionic liquids possess both Brønsted and Lewis acid sites and Lewis acidity strength increased with the increasing content of Lewis acid sites. Studies on acidity-activity relationship revealed that the acidity order was accordant with that of catalytic activity. Further studies on the scope and applications of the Brønsted-Lewis acidic ionic liquids are now underway in our laboratory.

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